Temperature effects on the infrared spectrum of molecules in planetary nebulae

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Abstract. In this work, we utilize a method based on Wang-Landau Monte Carlo sampling for studying the temperature effects of astrophysically relavant molecules. Anharmonic effects, e.g., resonances, overtones, and combination bands, are fully incoporated in this method. The calculated infrared (IR) spectra are consistent with the experimental data measured by National Institute of Standards and Technology (NIST).

Keywords. PAH, molecule, infrared, temperature, anharmonic, spectrum

1. Introduction

IR spectroscopy is a powerful tool to study molecules in space (Tielens, 2008). A key issue in such analysis is understanding the effect that temperature has on different vibrational bands, and thus interpret the IR spectra for molecules in various media. From the theoretical point of view, the effect of temperature on IR vibrational spectra depends on anharmonic effects and can be accounted for using several methods, e.g. applying empirical scaling factor on the harmonic frequencies (Merrick, 2007); classical molecular dynamics simulations (Van-Oanh, 2005), Car-Parrinello (Kumar, 2006) and Born-Oppenheimer molecular dynamics (Estácio, 2008), etc.

Alternatively, temperature effects on the IR spectra can be incoporated through inverse Laplace transformation of quantum partition functions (Romanini, 1993). In such a method, the vibrational Density of States (DoS) are estimated by direct Monte Carlo (MC) integration. However, such methods become highly inefficient for large systems due to increasing variances (Hüpper, 1999). An improved MC method, the Wang-Landau method is introduced for handling high-dimensional space problems. It has been shown that such a method could reproduce very accurate vibrational DoS for large, nonseparable systems (Basire, 2008).

We apply this Wang-Landau method on theoretical spectra at 0 Kelvin (calculated by second-order Vibrational Perturbations Theory (VPT2) (Mackie, 2015), in such spectra all anharmonic effects, i.e., resonances, overtones, and combination bands, are fully incoporated.

2. Computational details

The infrared spectra at finite temperatures are calculated in three steps: first of all, we compute the vibrational DoS by the Wang-Landau method (Basire, 2008); secondly, we
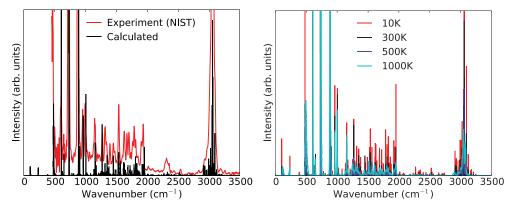
Figure 1. Gas phase IR spectra of anthracene ($C_{14}H_{10}$) molecule. The left panel compares the calculated and experimental spectra (recorded by NIST at 300K). The right figure compares the calculated spectra at different temperatures.

accumulate internal-energy dependent two-dimensional histograms of the intensities and energies of the transitions; finally, we convert the accumulated absorption histograms to microcanonical absorption spectra, which derives final the absorption intensities and energies at finite temperature through Laplace transformation. For details of the method, see Chen *et al.* (in preparation).

3. Results and Discussion

Several Polycyclic Aromatic Hydrocarbon molecules (PAHs) are tested with this method. Figure 1 shows the IR spectra of anthracene ($C_{14}H_{10}$) molecule. The left panel compares the calculated and experimental spectra (NIST at 300 K). It can be seen that the calculated spectrum is consistent with the experimental results. The right panel presents the spectra at different temperatures. Due to temperature effects, independent line shifts and broadenings can be observed clearly. Such spectra may guide infrared observations to detect PAH molecules in interstellar medium, and also aid in deeper understanding of measured spectra. For more results and discussion, see Chen *et al.* (in preparation).

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